

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: **0 463 660 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91201382.8**

(51) Int. Cl.⁵: **A23L 1/226, C11C 3/00**

(22) Date of filing: **05.06.91**

(30) Priority: **22.06.90 EP 90306873**

(43) Date of publication of application:
02.01.92 Bulletin 92/01

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI NL SE

(71) Applicant: **QUEST INTERNATIONAL B.V.**
Huizerstraatweg 28
NL-1411 GP Naarden(NL)

(72) Inventor: **Simmons, John**
34W478 Country Club Road
St. Charles, Illinois 60174(US)
Inventor: **Visser, Jan**
Gooilandweg 144
NL-1271 LB Huizen(NL)

(74) Representative: **Hartong, Richard Leroy et al**
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) **Process for the preparation of flavouring mixtures.**

(57) The invention concerns a process for the preparation of flavouring mixtures by heating of fatty acids or fatty acid derivatives with an oxidizing agent in the presence of at least 0.1% by weight of an antioxidant. Polyunsaturated fatty acids or animal or vegetable fats which are rich in such acids are preferred as starting materials. The preferred oxidizing agent is oxygen. The oxidation mixtures obtained are rich in aldehydes and can be used to improve the organoleptic properties of foods.

EP 0 463 660 A1

The invention concerns a process for the preparation of flavouring mixtures through controlled oxidation of fatty acids. More particularly, the invention concerns a process for the preparation of such mixtures through oxidation of fatty acids or fatty acid derivatives in the presence of antioxidants. The invention also concerns flavouring mixtures obtainable thereby and flavouring compositions and foods containing these flavouring mixtures.

It is known in the art that the specific flavour of animal and vegetable fats and oils depends on the presence of minute quantities of compounds derived from oxidative degradation of these fats and oils. Saturated and unsaturated aliphatic aldehydes are among such oxidation products. From I. Hornstein in "The chemistry and Physiology of Flavours", The AVI Publishing Company, Inc. 1967, Chapter 10, it is known that the species-specific flavour of animal fats may be enhanced by heating in air. From J.E. Kinsella, Food Technology, May 1975, pp. 82-98 it is known that aliphatic aldehydes are important contributors to the flavour of butter, but that they give "oxidized" off-flavours when they accumulate above critical concentrations. Similar problems are known for other fats and oils, and antioxidants are often added to prevent undue oxidation, see e.g.: V.N. Wade et al, Milchwissenschaft 41 (8), 1969, pp.479-482 and Ch.N. Rao et al, Asian J. Dairy Res. 3 1984, pp. 127-130. EP 172 275 describes a process for preparing butter-like or animal-type flavourings by heating a mixture of enzyme modified milk fat and another fatty material. EP 298 552 describes the preparation of a flavour concentrate for imparting a butter-like flavour, prepared by oxidizing butter fat. The oxidized butter fats obtained thereby contain a few ppm's of aliphatic aldehydes with up to 9 carbon atoms.

On the other hand, aliphatic aldehydes and other compounds derived from fat degradation are known to play an important role in the flavour industry and are added in small quantities to a number of flavouring compositions and foods to impart or strengthen desirable flavour qualities. Therefore, there is a need for flavouring mixtures which are rich in such compounds.

It has now been found that flavouring mixtures which are rich in various aliphatic aldehydes and other flavour compounds derived from fat degradation may be obtained through controlled oxidation of fatty acids or fatty acid derivatives in the presence of antioxidants. The oxidation mixtures may either be used as such as flavouring mixtures, or the aldehydes and other compounds may be concentrated or separated from the oxidation mixtures to prepare more concentrated flavouring mixtures.

According to the invention a fatty acid or a fatty acid derivative is heated in the presence of an oxidizing agent and an antioxidant for a sufficient time and to a sufficiently high temperature to obtain a desired level of flavour compounds in the oxidation mixture.

Fatty acids as used in this invention are aliphatic carboxylic acids having between 4 and 26 carbon atoms, preferably more than 14 carbon atoms. Mono- and especially poly-unsaturated fatty acids or mixtures which are rich in these acids are preferred. Fatty acid derivatives comprise fatty acid salts, especially those of alkali or alkali earth metals, and fatty acid esters of mono- or polyhydric alcohols. Examples of such esters are ethyl esters, esters of long chain aliphatic alcohols such as those found in certain natural waxes (like beeswax) and oils (like jojoba oil) and mono-, di- or triesters of glycerol such as animal or vegetable solid or liquid fats (the latter are usually referred to in the art as oils). Examples of animal fats are: tallow, milk fat, lamb fat, chicken fat, egg fat and fish oils. Examples of vegetable fats are: olive oil, sunflower oil, coconut oil, peanut oil, sesame oil, palm oil, palm kernel oil, linseed oil, safflower oil, soy bean oil, avocado oil, almond oil, hazelnut oil, evening primrose oil, etc. Fats which are relatively rich in unsaturated, particularly poly-unsaturated, fatty acids are preferred. Also preferred are fats containing branched chain fatty acids, which are present in relatively small quantities in some fats. Animal or vegetable fats may either be used as such in the process of the invention or they may first be subjected to chemical or enzymatic hydrolysis. In that case either the fatty acids are first isolated from the hydrolysis mixture, or the hydrolysis mixture as such is used in the process of the invention. Depending on the reaction conditions used for the hydrolysis, this reaction may even be combined with the process of the invention. Particularly preferred fatty acids are linoleic, linolenic and arachidonic acid; particularly preferred fats are those which are rich in one or more of these fatty acids.

Oxidizing agents used in the process may be oxygen, hydrogen peroxide (or a source thereof), ozone, oxidizing metal ions such as Cu^{2+} or Fe^{3+} , or suitable combinations of these oxidizing agents. When oxygen is used, it may be either pure oxygen or a mixture of oxygen with an inert gas. For reasons of convenience air is preferred as the oxygen source.

Antioxidants suitable for the process of the invention are either single compounds, or mixtures of compounds which are generally recognized to prevent or retard oxidation. Preferred are antioxidants which are permitted by food regulations to be present in or added to foods, in particular in/to fats. Especially preferred are butylated hydroxytoluene, butylated hydroxy-anisole, gallate esters, tocopherols, tocotrienols, ascorbic acid and its salts and esters such as ascorbyl palmitate. Particularly preferred are tocopherols. The

antioxidant should be present in a quantity of at least 0.1% by weight based on the quantity of fatty acid or fat. Preferably, the antioxidant is present in a quantity of 0.5% or more, particularly 1% or more. It could be as high as 100% but higher quantities than 50% are rarely useful. These antioxidant quantities refer to the quantity actually added to the reaction mixture over and above any anti-oxidant which may already be present naturally in the fatty acid or fat. Generally such antioxidants are present naturally only in quantities which are negligible compared to the quantities used in this invention

The temperature at which the controlled oxidation is carried out is not critical: To complete the process within a reasonable time span preferably a temperature of 30 °C or more, more preferably 50 °C, particularly 65 °C or more is used. With special precautions temperatures as high as 350 °C could be used, but in most cases the quality of the flavour mixtures obtained is affected due to undesirable side reactions at temperatures higher than 180 °C. The process is generally carried out below 125 °C.

The heating time is dependent on the temperature used and the level and ratio of aldehydes desired. A heating time of only 30 sec may be sufficient at very high temperatures, whereas at a temperature near 30 °C heating times up to 100 hours may be necessary. Generally heating times between 1 and 20 hours are satisfactory.

The controlled oxidation may be carried out on the fatty acid, fatty acid mixture or fat as such, or a suitable reaction medium may be added. Particularly suitable reaction media are water and other polar solvents e.g. polyols such as glycerol and propylene glycol, or solutions of an alkali or alkali earth metal salt of a mineral acid such as sodium or potassium chloride in any of these solvents. Such reaction media can be used in quantities of up to 95%, particularly up to 50% by weight of the total oxidation mixture. Preferably a quantity of 20% or more is used. The oxidation reaction can be carried out at a pH between 1 and 10, preferably the pH should be between 2.5 and 8.

The reaction may be carried out by simply heating the reaction mixture in an open or closed reaction vessel, whilst agitating it by any suitable means such as stirring, shaking, vibration, etc. A closed vessel should always be used if the reaction temperature is above the boiling point at atmospheric pressure of the reaction medium. When an open vessel is used, care should be taken not to lose volatile aldehydes in the atmosphere, e.g. by using a reflux condensor or a cold trap. Oxygen may be conveniently supplied by bubbling an oxygen containing gas mixture such as air through the reaction mixture, or by dispersing atmospheric oxygen through the reaction mixture by any of the agitating means mentioned above.

As outlined above, the oxidation mixtures obtained by the process of the invention are valuable flavour mixtures due to their high content of aliphatic flavour aldehydes and other flavour components. Such aldehydes include: n-pentanal, n-hexanal, n-heptanal, n-nonanal, cis-3-hexenal, trans-2-nonenal, trans-2-decenal, cis,trans- and trans,trans-2,4-heptadienal, cis,trans-trans,trans- and trans,cis-2,4-decadienal. Other flavour components may include aliphatic ketones, lactones and relatively short chain fatty acids. Which of these aldehydes and other components are present in a particular flavour mixture and in which quantities and ratios depends on the fatty acid or fat starting material, taking into account that the results of mixtures of fatty acids or fats can be different from the sum of the results of the separate components, due to preferential oxidation of certain fatty acids over others. The composition of the flavour mixtures is also dependent on the type and quantity of antioxidant and on the reaction conditions used such as time, temperature, mixing efficiency or amount of oxygen supplied. By changing these variables the flavour properties of the flavour mixtures may be varied to suit specific needs. In most cases it is preferred that the reaction medium is saturated with oxygen during the reaction. The process of the invention is particularly useful in providing flavouring mixtures with a relatively high content of poly-unsaturated aldehydes.

The oxidation mixtures obtained as described above can be used as such, but they can also be converted into more concentrated flavouring mixtures by separating the flavour components from part or all of the fatty acids or fat which is still present, or they can be fractionated to give other flavouring mixtures containing different quantities and/or ratios of flavour components, or even to give single flavour components. Such separation, concentration, or fractionation may be carried out using methods known in the art such as distillation, steam-distillation, co-distillation with a suitable solvent such as triacetone, diacetone, or triethylcitrate, fat removal by crystallisation from a suitable solvent such as isopropanol, extraction e.g. with ethanol, chromatographic techniques, etc.

The flavouring mixtures according to the invention may be added as such to foods or they may first be combined with a suitable diluent or carrier or be converted into powdered products e.g. by spray drying or other encapsulation techniques known in the art. In many cases it is advantageous to combine the flavouring mixtures with other flavouring ingredients into flavouring compositions. The flavouring mixtures may be very suitably combined with flavouring ingredients obtained by Maillard- or Amadori-type reactions between sugars and aminoacids and/or sulphur compounds. Such combination may be made after the Maillard-reaction has taken place. In another embodiment the starting materials for the flavouring mixture of

the invention may be added before or during the Maillard reaction so as to have the Maillard reaction and the fatty acid oxidation taking place simultaneously.

The term "flavouring composition" is used here to mean a mixture of flavouring ingredients of natural and/or synthetic origin, if desired dissolved in a suitable solvent or mixed with a powdered substrate, or processed into a powdered product, which is used to impart a desired flavour to foods. The term "food" is used here to mean a solid, semi-solid or liquid product intended for oral consumption by man or animals. Flavouring ingredients which may be used in conjunction with the flavouring mixtures according to the invention are well known in the art and are mentioned e.g. in S. Arctander, *Perfume and Flavor Materials of Natural Origin*, Elizabeth, N.J., U.S.A. (1969), in T.E. Furia et al., *CRC Fenaroli's Handbook of Flavor Ingredients*, 2nd ed., Cleveland, CRC Press Inc. (1975), in H.B. Heath, *Source Book of Flavors*, The Avi Publishing Co. Inc., Westport, Connecticut (1981) and in "Flavor and Fragrance Materials - 1989", Allured Publ. Corp., Wheaton, IL, USA.

The flavouring mixtures according to the invention or flavouring compositions containing them are particularly suitable to improve the organoleptic quality of foods and food components which need, or already have a fatty, creamy or dairy-type flavour, such as soups, sauces, gravies, dressings, meat products, snacks, shortenings, margarines, spreads, dairy-type products including products containing butter fat substitutes, bakery products, confectionary products. Some oxidation mixtures of the invention may even be used as ingredients with improved odour properties in perfumery and cosmetics. The invention is illustrated by the following examples but not in any way limited thereto.

EXAMPLES

In all tables the antioxidant content is in % by weight and the aldehyde content in ppm by weight of the fatty acid(s) or fat.

Example 1

The following general procedure was used for preparing the oxidation mixtures of tables 1-4 using the indicated fatty acids or acid mixtures:

To a mixture of 50g fatty acid(s) and 25 g water in a 300ml Erlenmeyer flask is added the quantity of Tocopherol concentrate 4-50 (a 50% solution in palm oil of a mixture of tocopherols which is rich in α -tocopherol, marketed by Jan Dekker, Wormerveer, The Netherlands) to supply the indicated concentration of tocopherols relative to the fatty acid(s) in the oxidation mixture. The mixture is shaken under air in a laboratory shaker whilst heating to 85 °C for 8.0 hours. After cooling the aqueous layer was separated and the fatty acid layer was analysed for its aldehyde content by gas chromatography, using an external standard, on a Carlo Erba GC 6000 equipped with a 25m x 0.3mm WCOT fused silica column FFAP CB df=0.29 μ m, of Chrompack International B.V., Middelburg, The Netherlands; column temp: programmed (4 °C/min) 80-240 °C; detector temp: 260 °C; injector temp: 250 °C; carrier gas: helium. The results are outlined in the tables 1-4 below

Table 1: Linoleic Acid; 85°C; 8 hours

tocopherol	0.25	0.50	1.00	2.00	4.00	8.00
hexanal	80	80	100	120	50	70
c,t-2,4-decadienal	60	60	70	80	100	120
t,t-2,4-decadienal	160	140	150	160	100	100

Table 2: Linolenic Acid; 85°C; 8 hours

tocopherol	0.25	0.50	1.00	2.00	4.00	8.00
cis-3-hexenal	50	50	70	100	170	390
c,t-2,4-heptadienal	60	60	140	160	520	830
t,t-2,4-heptadienal	100	90	120	120	200	300

Table 3: Oleic Acid; 85°C; 8 hours

tocopherol	0.25	0.50	1.00	2.00	4.00	8.00
nonanal	40	60	60	70	60	50
t-2-decenal	60	50	50	60	50	50

Table 4:

Oleic : Linoleic : Linolenic acid = 1:1:1; 85°C; 8 hours

tocopherol	0.25	0.50	1.00	2.00	4.00	8.00
hexanal	60	100	90	110	70	120
c-3-hexenal	20	30	30	50	130	210
nonanal	20	40	30	40	30	40
c,t-2,4-heptadienal	20	30	30	60	240	290
t,t-2,4-heptadienal	40	40	40	50	110	120
t-2-decenal	30	40	30	40	40	40
c,t-2,4-decadienal	40	60	50	50	90	80
t,t-2,4-decadienal	110	170	130	110	90	80

Example 2

Four 20g 1:1:1 mixtures of oleic, linoleic and linolenic acid with 10g water were oxidized in the presence of the 4 different antioxidants listed in table 5 below, using the procedure of Example 1. In each case the antioxidant concentration was 4% based on the weight of the fatty acids. " α -tocopherol" was Tocopherol concentrate 4-50. " δ -Tocopherol" was obtained from Jan Dekker, Wormerveer, The Netherlands and is a tocopherol mixture which is rich in δ -tocopherol. The resulting oxidation mixtures were analysed for their aldehyde content and the results are presented below.

Table 5: Fatty acid mix 1:1:1; 85°C, 8 hours

antioxidant	BHA	C8-Gallate	δ -tocopherol	α -tocopherol
hexanal	230	140	130	220
c-3-hexenal	150	80	60	140
nonanal	50	60	80	70
c,t-2,4-heptadienal	190	50	70	180
t,t-2,4-heptadienal	100	50	60	120
tr-2-decenal	80	60	70	90
c,t-2,4-decadienal	190	60	110	190
t,t-2,4-decadienal	210	50	150	270

Example 3

Three fatty acid mixtures according to Example 2 were oxidized as mixtures of 20g fatty acids with 10g of either water, 10% by weight aqueous NaCl solution or 25% NaCl solution respectively, using the procedure of Example 1. The mixtures all contained tocopherol (added as Tocopherol concentrate 4-50) in a concentration of 4% by weight of the fatty acids. The oxidation mixtures obtained were analysed and the results are given in table 6 below.

Table 6: Fatty acid mix 1:1:1; 85°C, 8 hours

aqueous phase	water	10% NaCl	25% NaCl
hexanal	220	130	110
c-3-hexenal	140	70	50
nonanal	70	60	60
c,t-2,4-heptadienal	180	70	70
t,t-2,4-heptadienal	120	70	60
t-2-decenal	90	60	60
c,t-2,4-decadienal	190	120	120
t,t-2,4-decadienal	270	210	180

Example 4

Mixtures of 20g peanut oil and 10g water were oxidized using the procedure of Example 1, in the

presence of Tocopherol concentrate 4-50 in quantities to give the tocopherol concentrations indicated in table 7. The aldehyde contents are given below.

Table 7: Peanut oil; 85°C; 8 hours

tocopherol	0.1	1.0	10.0
hexanal	60	130	150
nonanal	-	50	20
2-decenal	-	-	90
c,t-2,4-decadienal	460	1120	1680
t,t-2,4-decadienal	730	1970	2160

Example 5

Mixtures of 20g sardine oil and 10g water were oxidized using the procedure of Example 1, in the presence of Tocopherol concentrate 4-50 in quantities to give the tocopherol concentrations indicated in table 8. The aldehyde contents of the oxidation mixtures are presented below in table 8.

A fatty acid mixture was obtained by alkaline hydrolysis of sardine oil followed by acidification and separation of the fatty acids from the remainder of the hydrolysis mixture. 100g quantities of this fatty acid mixture were oxidized in the presence of different tocopherol concentrations as outlined above. The aldehyde contents of the oxidation mixtures are likewise presented in table 8 under "hydrolysed sardine oil".

Table 8: (Hydrolysed) sardine oil; 85°C; 8 hours

	Sardine oil			Hydr. sardine oil		
	0.1	1.0	10.0	0.1	1.0	10.0
tocopherol	0.1	1.0	10.0	0.1	1.0	10.0
c-3-hexenal	230	130	200	300	360	1180
c,t-heptadienal	260	530	1610	100	190	1770
t,t-heptadienal	240	200	240	120	140	250
t,c-2,4-decadienal	220	450	1260	150	300	1710

Example 6

Mixtures of 20g chicken fat and 10g water were oxidized using the procedure of Example 1, in the presence of Tocopherol concentrate 4-50 in quantities to give the tocopherol concentrations indicated in table 9. The aldehyde contents of the oxidation mixtures are presented below in table 9.

Table 9: Chicken fat; 85°C; 8 hours

tocopherol	0.10	0.5	1.0	4.0
hexanal	80	90	80	110
nonanal	-	50	80	-
2-decenal	80	70	80	90
c,t-2,4-decadienal	280	550	850	1330
t,t-2,4-decadienal	840	1200	1690	2090

Example 7

Mixtures of 20g linseed oil and 10g water were oxidized using the procedure of Example 1, in the presence of Tocopherol mix 4-50 in quantities to give the tocopherol concentrations (based on the quantity of linseed oil) indicated in table 10.

The aldehyde contents of the oxidation mixtures are presented below in table 10. The oxidation mixture obtained with 50% tocopherol present also contains oxidation products from the palm oil used as the solvent for the tocopherol and present in a quantity half that of linseed oil. However, due to the much larger proportion of poly-unsaturated fatty acids in linseed oil, the oxidation products in the oxidation mixture will be primarily derived from linseed oil fatty acids.

A fatty acid mixture obtained by hydrolysis of linseed oil (commercially available from Sherex Chemicals, Dublin, Eire) was oxidized in 20g quantities with 10g water in the presence of different tocopherol concentrations as outlined above. The aldehyde contents of the oxidation mixtures are likewise presented in table 10 under "hydrolysed linseed oil".

Table 10: (Hydrolysed) linseed oil; 85°C; 8 hours

	hydr. linseed oil				linseed oil			
tocopherol	0.1	1.0	10.0	50.0	0.1	1.0	10.0	50.0
hexanal	30	30	60	80	100	110	20	70
c-3-hexenal	70	110	630	880	260	320	280	400
nonanal	10	10	30	-	60	70	-	140
c,t-2,4-heptadienal	60	90	1080	1640	550	2250	3700	5070
t,t-2,4-heptadienal	100	140	410	560	580	860	550	670
t-2-decenal	10	20	10	-	70	50	-	-
c,t-2,4-decadienal	20	20	30	50	210	510	370	400
t,t-2,4-decadienal	60	70	40	30	550	880	520	450

Example 8

Mixtures of 20g chicken fat and 10g water were oxidized in the presence of different tocopherol concentrations and at different temperatures as described in Example 6, however, using a lower shaking speed. The contents of hexanal and 2,4-decadienals in the oxidation mixtures are presented in table 11.

Table 11: Chicken fat; different temps.; 8 hours

tocopherol	0.1	1.0	10.0
70°C			
hexanal	11	13	16
c,t-decadienal	100	230	240
t,t-decadienal	230	330	290
85°C			
hexanal	12	40	60
c,t-decadienal	140	490	930
t,t-decadienal	290	830	1130
95°C			
hexanal	30	30	120
c,t-decadienal	200	590	1010
t,t-decadienal	500	900	1230

Example 9

Mixtures of 20g tallow and 10g water were oxidized using the procedure of Example 1, but at a temperature of 96°C, in the presence of Tocopherol concentrate 4-50 in quantities to give the tocopherol concentrations indicated in table 12 (column 1 corresponds to no tocopherol added). The aldehyde contents of the oxidation mixtures are presented below in table 12.

Table 12: Tallow; 96°C; 8 hours

tocopherol	0	0.1	1.0	10.0
hexanal	10	4	7	10
nonanal	10	±3	±2	±3
c-2-decenal	10	±4	±5	11
c,t-2,4-decadienal	10	10	30	60
t,t-2,4-decadienal	15	15	50	60

Example 10

Mixtures of 20g lard and 10g water were oxidized using the procedure of Example 1, but at a temperature of 96°C, in the presence of Tocopherol concentrate 4-50 in quantities to give the tocopherol

concentrations indicated in table 13 (column 1 corresponds to no tocopherol added). The aldehyde contents of the oxidation mixtures are presented below in table 13.

Table 13: Lard; 96°C; 8 hours

tocopherol	0	0.1	1.0	10.0
hexanal	90	17	50	50
nonanal	50	±10	20	20
c-2-decenal	120	20	50	50
c,t-2,4-decadienal	140	30	170	340
t,t-2,4-decadienal	220	40	250	430

Example 11

Two oxidation mixtures were made, each of 120g of the fatty acid mixture of sardine oil referred to in Example 5, 60g of water and 24g of tocopherol concentrate 4-50 (10% tocopherol on fatty acids). Both mixtures were heated at 85°C for 8 hours in an open vessel equipped with a reflux condensor. One mixture was stirred while air was bubbled through; the other mixture was only stirred so as to aerate the oxidation mixture with oxygen from the atmosphere. After cooling the fatty acid layers were analysed as indicated in Example 1. The results are presented in table 14 below and show the influence of the quantity of oxygen present during the oxidation process.

Table 14:

Hydrolysed sardine oil; 85°C; 8 hours; 10% tocopherol

	bubble	stirr
cis-3-hexenal	90	160
c,t-2,4-heptadienal	380	200
t,t-2,4-heptadienal	110	50
t,c-2,4-decadienal	600	200

Example 12

Mixtures of 20g sardine oil and 10g glycerol were oxidized using the procedure of Example 1, but at a temperature of 96°C, in the presence of Tocopherol concentrate 4-50 in quantities to give the tocopherol concentrations indicated in table 15 (column 1 corresponds to no tocopherol added). The aldehyde contents of the oxidation mixtures are presented below in table 15.

Table 15: Sardine oil; 96°C; 8 hours.

tocopherol	0	0,1	1.0	10.0
c-3-hexenal	120	90	100	120
c,t-2,4-heptadienal	80	90	190	580
t,t-2,4-heptadienal	90	80	110	100
t,c-2,4-decadienal	170	170	300	720

Example 13

Mixtures of 20g chicken fat and 10g glycerol were oxidized using the procedure of Example 1, but at a temperature of 96°C, in the presence of Tocopherol concentrate 4-50 in quantities to give the tocopherol concentrations indicated in table 16. The aldehyde contents of the oxidation mixtures are presented below in table 16.

Table 16: Chicken fat; 96°C; 8 hours

tocopherol	0.1	1.0	10.0
hexanal	9	6	16
c,t-2,4-decadienal	90	180	310
t,t-2,4-decadienal	170	270	380

Example 14

Mixtures of 20g of fatty acids derived from sardine oil (as described in Example) 5 and 10g of water, glycerol or propylene glycol respectively were oxidized using the procedure of Example 1, but for a period of 5 hours, in the presence of 4g Tocopherol concentrate 4-50 (10% tocopherol on fatty acids). The aldehyde contents of the oxidation mixtures are presented below in table 17.

Table 17: Hydrolysed sardine oil, 85°C; 5 hours

reaction medium	water	glycerol	prop.glycol
c-3-hexenal	380	500	320
c,t-2,4-heptadienal	890	1060	780
t,t-2,4-heptadienal	100	160	90
t,c-2,4-decadienal	1140	1260	1080

Example 15

Mixtures of 20g sardine oil and 10g water were oxidized in the presence of different tocopherol concentrations and at different temperatures as described in Example 5, however, using a lower shaking speed. The aldehyde contents in the oxidation mixtures are presented in table 18.

Table 18: Sardine oil; different temps.; 8 hours

5	tocopherol	0,1	1	10
			70°C	
	c-3-hexenal	90	110	120
10	c,t-heptadienal	170	340	330
	t,t-heptadienal	100	80	60
	t,c-dekadienal	330	530	540
15			85°C	
	c-3-hexenal	140	180	210
	c,t-heptadienal	190	590	1310
20	t,t-heptadienal	160	210	180
	t,c-dekadienal	290	840	1410
			96°C	
25	c-3-hexenal	140	170	150
	c,t-heptadienal	190	470	1030
	t,t-heptadienal	170	210	180
30	t,c-dekadienal	370	560	1650

Example 16

35 Mixtures 100g of a fat or fatty acid from the list below, 50g of water and 2g of Tocopherol concentrate 4-50 (1% tocopherol on fatty acid or fat) were stirred and heated under reflux for 2 hours, whereafter the aqueous layer was separated. The resulting flavouring mixtures were assessed organoleptically by three trained flavourists and found to be very different from the starting fats and fatty acids. Their comments are
40 presented below:

45	Avocado oil	fresh, sweet, fruity, orange-like
	Oleic acid	sweet, fatty, fish-like
	Linoleic acid	sweet, fatty, chicken-like
	Linolenic acid	green, fatty, aldehydic
50	Peanut oil	chicken-like
	Almond oil	fatty, nutty
	Evening primrose oil	strong buttery, chicken, egg-like
	Maize oil	chicken-like, fatty
	Sardine oil	strong fishy, creamy, fatty
55	Butter fat	sweet, creamy, butter/cheese-like
	Chicken fat	strong chicken-like, fatty
	Hazelnut oil	fatty, hazelnut-like
	Coconut oil	like boiled potato skins
	Sunflower oil	clean chicken-like
	Joboba oil	fresh, nutty, sweet and cinnamon-like
	egg yolk fat	strong egg-like

Example 17

A dry chicken flavouring for soup was prepared by heating the following ingredients to reflux for two hours:

5	Enzymatically treated chicken meat powder	200g
	Glucose	40g
	Cysteine.HCl	40g
	Dry Yeast extract YEP 77 (1)	400g
10	Water	700g
	Chicken fat flavouring mixture of Table 9, col. 4	<u>100g</u>
	Total	980g

Thereafter 200g Paselli (2) and 500g water were added and the whole mixture was spray dried on a Büchi laboratory spray drier using an inlet temp of 180°C and an outlet temp of 90°C.

A cream soup base was prepared by mixing:

20	Perfectamyl P10X (2)	250g
	Paselli MD 20 (2)	300g
	Bouillon flavour 1006 (3)	30g
25	Yeast extract powder V/OC (1)	7g
	Salt	50g
	Monosodium glutamate powder, 1aq	18g
30	Cream powder DP 30-313 (4)	325g
	Melted chicken fat (37°C)	<u>20g</u>
	Total	1000g

110g of this mixture was dissolved in 11 of boiling water. To this soup base was added 10g of the dry chicken flavouring obtained above to give a chicken soup with a full bodied chicken flavour.

(1) Distillers Comp (Yeast) Ltd, Menstrie, Scotland

(2) AVEBE, Veendam, The Netherlands

(3) Quest International, Naarden, The Netherlands

(4) DMV-Campina, Veghel, The Netherlands

Example 18

A dry fish flavouring for soups and sauces is prepared as follows:

50g fish powder, 20g monosodium glutamate 1aq, 5g cysteine HCl and 125g water are mixed and heated under reflux for one hour. 2g of the treated sardine oil of table 8, column 3 is added and mixed through, followed by 20g Paselli and the whole mixture is spray dried on a Büchi laboratory spray drier using an inlet temp. of 180°C and an outlet temp. of 90°C.

Example 19.

A dry chicken flavouring for ragout is prepared by mixing 30g enzyme treated chicken meat powder, 4g cysteine HCl, 0.1g thym extract powder and 30g of Condimex 302 (a yeast-based HVP replacer marketed by Quest International). To this mixture is added 1g of a concentrated flavouring mixture prepared by extracting 100g of the sunflower oil flavouring mixture of Example 16 three times with 50 ml ethanol followed by concentrating this extract to 10 ml.

Claims

1. Process for the preparation of flavouring mixtures through oxidation of fatty acids or fatty acid derivatives characterized in that fatty acids or fatty acid derivatives are heated in the presence of an oxidizing agent and at least 0.1% by weight of an antioxidant for a sufficient time and to sufficiently high temperature to obtain a desired level of flavour compounds in the oxidation mixture.
2. Process according to claim 1 characterized in that a hydrolyzed animal or vegetable fat is used as a source of fatty acids.
3. Process according to claim 1 or 2 characterized in that poly-unsaturated fatty acids or mixtures rich in poly-unsaturated fatty acids are used.
4. Process according to claim 1 characterized in that the fatty acid derivatives are animal or vegetable fats.
5. Process according to claim 4 characterized in that a fat which is rich in poly-unsaturated fatty acids is used.
6. Process according to any one of claims 1-5 characterized in that oxygen is used as the oxidizing agent.
7. Process according to any one of claims 1-6 characterized in that the temperature is kept between 30 and 350 °C.
8. Process according to claim 7 characterized in that the temperature is kept between 50 and 180 °C.
9. Process according to claim 8 characterized in that the temperature is kept between 65 and 125 °C.
10. Process according to any one of claims 1-9 characterized in that the heating time is 30 seconds - 100 hours.
11. Process according to claim 10 characterized in that the heating time is 1-20 hours.
12. Process according to any one of claims 1-11 characterized in that a polar solvent, or a solution of an alkali or alkali earth metal salt of a mineral acid in such solvent, is present as a reaction medium in a quantity of up to 95% by weight of the total oxidation mixture.
13. Process according to claim 12 characterized in that the polar solvent is water, glycerol or propylene glycol.
14. Process according to claims 12 or 13 characterized in that the quantity of reaction medium is 20-50% by weight of the total oxidation mixture.
15. Process according to any one of claims 1-14 characterized in that the antioxidant is chosen from butylated hydroxytoluene, butylated hydroxy-anisole, gallate esters, tocopherols, tocotrienols, ascorbic acid or ascorbic acid derivatives.
16. Process according to claim 15 characterized in that the antioxidant is chosen from tocopherols, butylated hydroxy-anisole or gallate esters.
17. Process according to any one of claims 1-16 characterized in that at least 0.5 % by weight of antioxidant is present.
18. Process according to any one of claims 1-17 characterized in that flavour components are separated from part or all of the fatty acids or fat in the oxidation mixture.
19. Flavour components separated from flavouring mixtures obtainable by a process according to any one of claims 1-18.

20. Flavouring compositions comprising flavouring mixtures obtainable by a process according to any one of claims 1-18.

21. Foods comprising flavouring mixtures or flavour components obtainable by a process according to any one of claims 1-18.

5

10

15

20

25

30

35

40

45

50

55



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 20 1382

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A,	EP-A-0 298 552 (UNILEVER NV) * abstract; page 6, lines 1-30, claims 1-10 * - - - -	1,4	A 23 L 1/226 C 11 C 3/00
A	EP-A-0 295 509 (SOCIETE DES PRODUITS NESTLE S.A.) * abstract; claims 1-8 * - - - -	1	
A	CH-A-5 783 11 (SUNTORY LTD. et al.) * claims 1,2 * - - - -	1,4	
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 75 (C-55)(747), 19 May 1981; & JP - A - 5624484 (SANSHIYOU SEIYAKU K.K.) 09.03.1981 - - - - -	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 23 L 1/00 C 11 C 3/00
The present search report has been drawn up for all claims			
Place of search Berlin		Date of completion of search 22 August 91	Examiner SCHULTZE D
<div><div>CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div><div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</div></div>			